Assessment of the delivery of citronella oil from microcapsules supported on wool fabrics

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ABSTRACT

Essential oils are complex, volatile liquid mixtures that can be extracted from various parts of plants. Their main characteristics are strong fragrance and biological properties. Studying the characteristics of oils along with the possibility of an interaction with textiles creates new possible uses of this material. However, when oil is applied to a textile substrate, it is necessary to develop an oil release model, while most of the works only explore the application procedure and the fixed oil durability against washes. Thus, this work reports the mechanism and kinetics of controlled release of microencapsulated citronella oil from wool. The microencapsulation was done by complex coacervation with gelatin and gum Arabic biopolymers as shell materials. Optical microscopy, scanning electron microscopy and Fourier-transform infrared spectroscopy were used to confirm the encapsulation. The microcapsules were then supported by foulard in wool, fixed on fabrics and evaluated by attenuated total reflection Fourier-transform infrared spectroscopy. The controlled release of citronella from the microcapsules deposited on the fabric was studied *in vitro*. The microcapsules formed had a multi-core structure, and when applied to wool they showed diffusion by a Fickian mechanism in the first release stage and on the second stage changed to non-Fickian kinetics. The controlled release indicates that the textile structure influences the release model due to an interaction between fabric and water.

Keywords: wool; citronella; microcapsules; controlled release.

1. INTRODUCTION

Nowadays, consumers are interested in different functionalities in their clothing, and one of the fundamental attributes demanded is related with mosquito-repellent properties in textiles. Mosquitoes are responsible for the spread of diseases and illnesses to humans, such as Malaria, Yellow Fever, Dengue Fever and Zika virus. In recent years, various essential oils and their fragrances have been reported as mosquito repellents due to their eco-friendly and biodegradable nature [1].

Citronella oil is an example of this, and the Environmental Protection Agency (EPA) has classified the citronella oil as a biopesticide with a non-toxic mode of action, with concentrations ranging from 0.05% to 15% (w/v) [2,3]. In addition, the use of repellents derived from plants is an alternative to DEET (N, N-diethyl-m-methylbenzamide), since DEET has disadvantages, which include toxic reactions and skin damage.

On the other hand, some researchers report that this oil can be ineffective in combating insect vectors for reasons related to uncontrolled release, i.e., it is desirable that it be released in small amounts, providing long-term protection, since if released in large amounts, it will be of a short-time effectiveness [4]. An alternative to control the release is to microencapsulate the oil and apply it to the fabric compatible with the polymer used as the wall of the microcapsule. A fibre used for high quality products and featuring a variety of chemical groups is wool, besides being one of the most used natural textile biopolymers in industry [5].

The application of microencapsulation involving oils in textiles enables to extend the useful life of this material, preventing its rapid evaporation [6]. The microencapsulation provides stability to these compounds, allowing their controlled release under certain conditions [7]. The complex coacervation technique is used to microencapsulate, and it is based on specific interactions involving at least two polymers.

According to De Kruif, Weinbreck and Vries [8], the fundamental principle of formation of microcapsule through coacervation depends on the electrostatic interactions amongst opposing charges of molecules. On the other hand, this will be modified depending

on the pH, the type and amount of colloids, the charge ratio of both colloids, the chosen material and several other physical conditions, such as stirring, pressure and temperature [9].

The use of textile articles as supports for controlled release presents as properties to be highlighted: a high area of contact with the skin, drug loading capacity, ease of application, low price, release by stimulation, biocompatibility and to be non-allergic and non-toxic, among other properties [10-12]. The possibility to combine solid microstructures into a fabric structure allows the defined system to be controlled in two different ways: the characteristics of the microcapsule/microsphere and the physicochemical affinity between the fiber itself and the active principles [11,13,14].

The novelty of this work is the study of how the microcapsules are retained in the wool fiber and the modeling of the controlled release of the oil from the wool fabric using the Higuchi [15] and Korsmeyer et al. [16] kinetic models [17]. The release of citronella oil in a controlled manner has been the primary challenge for its application in the fight against vectors using textiles.

2. MATERIALS AND METHODS

2.2.1. Preparation of microcapsules by complex coacervation

Complex coacervation was carried out using the technique described extensively in several works [18-22]. The use of two biopolymers characterizes this procedure. First of all, one of the polymers is dispersed with the citronella oil, afterward, the pH is adjusted to activate the cationic charge of the first polymer, subsequently, the second polymer is added and, finally, a crosslinking agent. Figure 1 is a schematic representation of microcapsules produced by complex coacervation.

Figure 1. Diagram mechanism for the fabrication process of microcapsules containing citronella essential oil (core) by complex coacervation with gelatin and gum Arabic (GA:GE 1:1) as shell materials.

The procedure began with the formation of three emulsions, the first contained 3 g of gelatin in 50 mL of water, the second emulsion contained 5 mL of citronella essential oil and 0.3 g of sodium lauryl sulfate (SLS), the surfactant used to increase the dispersion of oil in the water, and the last emulsion was prepared with 100 mL of water and 3 g of gum Arabic. The three emulsions were prepared separately in aqueous solution at 50 °C, under stirring at 300 rpm [14] and the ratio GA:GE was 1:1 [21].

In the following stage, the first and the second emulsions were blended. Stirring was increased to 500 rpm to guarantee thorough dispersion of the oil and to obtain droplets of small diameter. Then, the third emulsion was added to the previous mixture, followed by an adjustment of pH to 4 using citric acid. The pH adjustment took into account the ratio 1:1 (GA:GE) and the mixture was left at rest for 90 minutes, until complete stabilization [19]. The resulting suspension was cooled to a temperature of <8 °C and remained unperturbed for 1 h. Then, the pH of this preparation was adjusted to 8–9 using NaOH (1M), and 1 g of glutaraldehyde (50%) was added dropwise. The pH was adjusted because the reaction mechanism of the aldehyde group with the amino group (cross-linking) is a reaction that should be carried out at a high pH for its optimization [20]. The system was left for 12 h under stirring at room temperature, resulting in microcapsules for application into fabric substrates [24].

2.2.2. Application to wool substrate

The application of the microcapsules in the fabric was carried out using the foulard (KIMAK) process with the pad-dry-cure technique [23, 24] at 85% of pick-up and followed by curing. Wool textiles were impregnated for 1 minute in a suspension of 30 g L^{-1} of microcapsules at 25 °C and pH 6. Then, the fabric has gone through a foulard at a pressure of 2 bar. After that step, microcapsules were fixed in the fabric using a solution of 1,2,3,4-butanetetracarboxylic acid (BTCA). Tetra-carboxylic acid as zero formaldehyde based cross-linker has drawn attention with regard to the treatment of wool [25], and this process was

conducted in the presence of sodium hypophosphite (SHP), used as a catalyst to condition the reaction. A durable finishing is obtained and consists of the cross-linking of the wool fibers and the microcapsules. Curing was performed at 180 °C for 1.5 min.

2.2.3. "In vitro" release behavior and mechanism

The release profile of citronella essential oil from the textile substrate was determined by the technique introduced by Ghaheh et al. [26], Labay et al. [27] and Carreras et al. [23] with some changes. After treatment with microcapsules, the wool fabric (3 x 6 cm) was placed in a thermostatic bath at 37.0 ± 0.5 °C, under stirring in a WNB14 shaker (Memmert) during 14 h, as previously described in the work performed by Bezerra et al. [28]. Aliquots of 2 mL were extracted at predetermined times and filtered. Their absorbance was determined by spectroscopy in the ultraviolet region, at 333 nm (oil), using a UV-240LPC (Shimadzu) equipment. A calibration curve for the oil concentration was constructed to determine the amount of active principle (citronellal compound) released into the water from the microcapsules at different times, Eq. 1:

$$C_{oil} = (abs_{333} - 0.0359)/12.66 \quad (1)$$

Where: C_{oil} is the oil concentration, mg mL^{-1}, and abs is the absorbance (fractional %) at the wavelength of 333 nm.

Mathematical fittings of the data to obtain the amount of citronella oil released from the microcapsule in the wool fabric were derived from the Higuchi zero-order and Korsmeyer et al. equations [15,16]. These models were chosen because they explain the release of microcapsules and complexes on flat surfaces, as is the case of textile substrates.

Higuchi's equation [15], Eq. 2, can be written as follows.

$$f = \frac{M_t}{M_\infty} = K_H t^{1/2} \quad (2)$$

Where $\frac{M_t}{M_\infty}$ is the percentage of oil released at each time point t relative to the percentage released in equilibrium and K is the Higuchi constant for oil release.

Higuchi's model of active principle release is based on Fick's law, called Fickian mechanism, dependent on the square root of time [29].

Alternatively, the Higuchi zero-order model is an indicator of controlled release by membrane diffusion, Eq. 3, which acts as a barrier to itself, i.e., it has a release burst represented by K_t:

$$f = \frac{M_t}{M_\infty} = K_t + K_H t^{1/2} \quad (2)$$

Korsmeyer et al. [16] created a simple semi-empirical model that relates the release of the active principle with the time elapsed raised to a constant. This equation, Eq. 4, can be written as follows:

$$f = \frac{M_t}{M_\infty} = K_{KP} t^n \quad (4)$$

K_{KP} is the Korsmeyer kinetics rate constant, which incorporates structural and geometric characteristics; *n* is the release exponent, an indicator of the mechanism, which, according to Table 1, is related to the release geometry [16].

Table 1. Release system related to Korsmeyer et al. [16] exponent n based on geometry as given by Carreras et al. [23].

SURFACE	CYLINDER	SPHERE	DIFFUSION MECHANISM
0.50	0.45	0.43	Fickian
0.50<*n*<1.00	0.45<*n*<0.89	0.43<*n*<0.85	Anomalous
1.00	0.89	0.85	Non-Fickian

The transport in swelling systems can be described by Fick's Second Law and, for short periods, the release can be studied as diffusion on a flat surface, from the Korsenmeyer–Peppas equation, Eq.5, approximation [22, 30, 31]

$$\frac{M_t}{M_\infty} = K_{KP}\sqrt{t} = 4\sqrt{\frac{D\ t}{\pi\ \delta^2}} \quad (5)$$

Where *D* is the diffusivity of the active principle in the polymeric system and δ is the thickness of the lamina.

For statistical analysis, triplicate data are presented as the mean ± of the standard deviation (SD). Statistical significance ($p<0.05$) was determined by one-way analysis of variance (ANOVA) using OriginPro version 8.5.1.

3. RESULTS AND DISCUSSION

3.1. Morphology and thermal properties

Figure 2 presents the microcapsules formed. The micrograph showed that the microcapsules were suspended in water, confirming the coacervation process. They exhibit a multi-disperse distribution and multiple cores. Obtaining a multi-core microcapsule hinders the escape of the active principle imprisoned due to the greater amount of walls, gelatin and gum Arabic. This will directly influence the mechanism of controlled release, as it is objectively applied on the longer release time, causes an increase in the functionality of the fabric. Yang et al. [32] show that multi-core microcapsules exhibit better controlled release compared to those with a single core because the former can slowly release the encapsulated active principle over time.

Figure 2. Micrograph of the emulsion extract shows the multi-core strucuture produced through complex coacervation and the coacervated microcapsule of citronella oil, GE/GA with MR 1:1,obtained by optical microscopy. Bar represents 20 µm.

According to Wang et al. [33], the formation of multiple cores occurs due to the formation of the wall by the gelatin and the bioactive ingredient in a first phase. After the change in pH from pH 4, the adsorption of the free coacervate dispersed in the aqueous phase occurs, resulting in the formation of microcapsules with multiple cores.

In Figure 3 it is possible to compare the thermogravimetric behavior of microcapsules with citronella oil (MO) (a) and void (MV) (b). The mass loss in the microcapsules can be divided into three steps (I, II and III) and in the void microcapsules into two steps (I and III).

Figure 3. Thermogravimetric analysis (TGA) gave the thermograms curves for citronella oil microcapsule (GE:GA 1:1) (a), void microcapsule (GE:GA 1:1) (b), and the derivative thermogravimetric analysis (dTGA) for microcapsules [black curve] and void microcapsules [red curve](c).

The first mass loss, stage I, was seen as the loss of moisture, both systems act similarly in relation to it. The second stage, ranging from 231.33 to 292.17 ºC for MO, is not seen in Figure 3 (b), MV, thus, this thermal event was seen as the breaking of the wall of the microcapsule and the loss of essential oil that is encapsulated in the polymeric systems, the mass loss was 57.68%.

The sudden decrease in mass can be attributed to the presence of the citronella oil, which is released from the breaking of the protective microstructure at a temperature higher than its boiling point. A similar result was obtained by Jain and co-workers [34] when they analyzed the differences in mass loss between the void microcapsules and β-carotene microcapsules, showing that the steep loss of mass was probably due to decomposition of the complex and oil release.

The last stage of mass loss, beginning at 297.80 ºC and extending up to 364.25 ºC for microcapsules and in the range of 240.50 to 417.40 ºC for void microcapsules, could be explained by the decomposition of wall materials, GA and GE. In Figure 3 (c) dTGA, it can be seen that the thermal decomposition events for the two microcapsules are similar.

And finally, it can be verified that MO present a lower residual mass, 9.22%, while MV presented 23.29%. This occurs due to the presence of citronella oil, because it presents high volatility and does not produce residuals. That difference is related to the capability and effectivity of the microencapsulation method.

3.2. Infrared spectroscopy (FTIR)

Figure 4 shows the FTIR analysis of the citronella oil, of the biopolymers used and of the microcapsule obtained. The FTIR spectrum of gelatin shows the presence of amide and amine. The bands identified are: 3,431.10 cm^{-1} ($CONH_2$), 1,631.71 cm^{-1} (primary amide C=O stretch), 1,543.40 cm^{-1} (secondary aromatic amide), 2,927.08 ($-NH_2$), 1,337.05 (deformation C-N) and 1,078.33 cm^{-1} (axial deformation of the aliphatic amine C-N) [33, 35]. The amino group belonging to the chain of gelatin has a positive charge in the acid medium due to the presence of a protonated amino group (NH_3^+) [36].

Figure 4. FTIR spectra of the: (a) gelatin; (b) citronella oil unencapsulated (c) gum arabic; (d) the coacervated microcapsule obtained .

As a result, the IR spectrum of citronella oil (3,7-Dimethyl-6-octenal) shows absorption bands at 2,715.02 cm^{-1} (aldehydic C–H stretch), 1,720.77 cm^{-1} (aldehyde carbonyl H-C=O), 1,645 (O–H), 1,377.96 (dimethyl angular deformation CH_3) [37]. The infrared spectrum of gum Arabic shows bands at 3,430 cm^{-1} (OH stretching), 1,616.02 cm^{-1} (axial vibration of the C=O) and at 1,419.40 and 1,252 cm^{-1}, which are two bands of axial deformation referring to the carboxylic acid (COOH) [32]. The presence of the protonated amino groups (NH_3^+) in the gelatin and deprotonated carboxyl group (COO^-) in the gum Arabic are essential for forming the microcapsules, the interaction between these two groups must form a novel amide bond that can be detected by means of FTIR.

The FTIR spectrum of the microcapsules shows bands similar to those of the FTIR of gelatin and gum Arabic [38,39]. However, the emergence of new bands at 1,636.74, 1,545.55 and 1,241.60 cm^{-1} is characteristic of the primary, secondary and tertiary amide groups [33]. These new bands show that the interaction between the carboxyl groups of the gum Arabic interacts with the amine groups of gelatin, this being another indication of the formation of MO.

3.3. Application to wool substrate

The results of the application of the microcapsules are shown in Table 2. The presence of microcapsules in the textile structure at the end of the process is confirmed. The amount of retained microcapsules (o.w.f) is 0.091 ± 0.005 %.

Table 2. Results of the finishing process with microcapsules

	Wool fabric
Mass (g)	0.209 ± 0.005
Pick-up (%)*	85 ± 1
o.w.f. (%)**	0.091 ± 0.005

*pick-up (%) theoretical percentage of product present after impregnation, wet fabric, with relation to the dry fabric

**o.w.f. (%) (on weight of fibers) amount of product applied, calculated by mass difference between the dry fabric untreated and dry fabric after the finish.

This result is associated with the chemical functionalities of wool and microcapsules, in addition to the new bonds created through the fixation reaction with BCTA [40]. Wool can perform various types of reactions, due to the chemical reactivity of glycine, serine, glutamic acid, cysteine and others.

Figure 5 shows the scanning electron microscopy of microcapsules in wool textile. In these micrographs, it is possible to observe the distribution of the multi-dispersed material, the small size of the microcapsules, and their dispersion. The morphology observed by optical microscopy is different from that observed in the SEM, it is noted that the microcapsule, when deposited on the surface of the fabric, forms agglomerates, probably because of the addition of the BTCA crosslinking agent used to increase the fabric@microcapsule interaction, as this also increases the interaction of microcapsule@microcapsule due to the esterification reaction. The SEM also indicated the suitability between gum Arabic and gelatin as a wall material for the encapsulation of citronella.

Figure 5. Scanning electron (a) wool fiber untreated and (b) micrographs of citronella oil microcapsules (GA/GE) applied on wool fiber using the foulard process and the paddry-cure-technique and BTCA as cross-linking agent, wool treated. Bar represents 30 μm.

Figure 5 also shows that there is a small proportion of microcapsules with a geometry not perfectly spherical, i.e., the image depicts them as elongated spheres, similar to the microcapsules found by Krishnan, Kshirsagar and Singhal [41]. This elongation is due to strong agitation during the coacervation phase, forming micelles with SLS. Leclerq et al. [20] showed that the limited concentration of negatively charged colloids, in this case gum Arabic, may also contribute to the change in the shape of the microcapsules. The small size of the microcapsules is usually related to the ratio between oil/polymer/SDS and the rate of stirring. The reduced size and the elongated shape facilitates absorption and penetration into the surface of the wool due to the occupation of fabric interstices, and these characteristics cause the microcapsule to have a larger surface area, allowing greater contact with the fabric, as seen in the SEM, the microcapsules cover the fiber.

3.4. Quantification and mathematical model for the fitting of the controlled release of citronella essential oil

The study of the drug delivery of the wool fabric with microcapsules of citronella was performed following the methodology explained in the section 2.2.4. Figure 6 shows the process of releasing the complex of citronella essential oil in the wool. It can be seen that the process takes place in two distinct stages, implying that the release of citronella oil in the system wool/microcapsules/water shows a transitional behavior.

Figure 6. In vitro controlled release profiles in water at 37 ^{o}C for microencapsulated applied on wool (a) modeling of the release profile by Higuchi-order zero; Higuchi and Korsmeyer-Peppas of citronella essential oil first step (b) and second step (c).

In the first interval, from 90 to 230 minutes, approximately 50% of the oil is released into the water from the system microcapsules/fabric. The outward zones of the microcapsule release oil in a well-ordered manner onto the fiber. During this step, the concentration

304 gradient in the inner zones of the microcapsule is changing due to the delivery of the oil onto
305 the fiber. Meanwhile, a secondary gradient is formed in the structure of the fabric and the
306 level of retention of the oil will depend on its affinity towards the fiber. Therefore, the balance
307 between both concentration gradients is what really promotes the second step in the delivery
308 process. As it can be seen in Fig. 6, at the end of the process, 100% of the oil that could be
309 released is delivered into water from the system microcapsule/fabric.

310 As expected from mass transport systems governed by two different gradients of
311 concentration, they have to show two different slopes that represent, to some extent, the two
312 rates of delivery. The first slope is less steep and, after 400 min, the amount of oil released
313 reaches the maximum. That behavior is a consequence of the slower delivery of the oil to the
314 fabric, and from there to the water. Due to this fact, the system can hardly be considered as
315 governed by microcapsules [42]. Since the profile had indicated two distinct regions of
316 release, adjustments were made in each of them (Figure 6) [42], Kormeyer-peppas release
317 profile was fitted only to values up to 0.6.

318 From the data analysis, it can be seen that in the first stage, the constant kinetic rate
319 was of 0.06 min^{-1}. Table 3 shows the adjusted models and the parameters resulting from the
320 fittings, according to Higuchi zero-order, Higuchi and Korsmeyer models.

321

322 **Table 3.** Parameters of the controlled release of citronella oil from the microcapsules,
323 modelled by Higuchi zero-order, Higuchi and Korsmeyer-Peppas models.

Model	Parameter	First stage	Second stage
Higuchi zero-order	R^2	0.9812	0.9661
	$K_0(10^{-2})$	-0.065±0.0862	0.0020±0.0003
	K_{H0}	0.0657±0.0044	0.0034±0.0061
Higuchi	R^2	0.9820	0.7558
	K_H	0.0625±0.0013	0.0406±0.0022
	$D_f(10^{-2})$	0.0767±0.0032	0.0324±0.0022
Korsmeyer-Peppas	R^2	0.9800	0,9667
	K_{KP}	0.06367±0.0058	0.0029±0.0001
	n	0.4930±0.0291	0.9516±0.07326

It is also seen in Table 3 that the respective functions used are suitable for the adjustment of the experimental results of the wool cloth, because all of them have coefficients of determination higher than or equal to 0.9800 in the first step of release. Comparing the fittings, the Higuchi model has the highest coefficient of correlation R^2=0.9820, while the Korsmeyer-Peppas model indicated R^2=0.9800, demonstrating that the first stage of release occurs by the Fickian mechanism shown in Table 1.

The Higuchi zero-order model considers the existence of an initial burst release, however, Table 3 shows the non-significant influence of the first constant of this model in the case of the release of citronella oil from the microcapsules. As shown in Table 3, for the first stage of release, the coefficients of determination have close values for the two Higuchi models, but with less statistical dispersion and a better fit for the zero-order model. As expected, the second stage shows a smaller coefficient of determination, a fact that corroborates our earlier analysis of the mechanism. Surathi and Karbhari [43] show that in this type of mechanism, the rate of diffusion of the active pinciple is lower than the mobility of the polymer chain segment, and for this reason, the mechanism depends only on diffusion.

In this case, the application of the Korsmeyer-Peppas model provided reliable results, because the first stage has shown n close to 0.5, meaning that the diffusion of oil governs the mechanism of release from the microcapsules. Furthermore, in the second stage, the value of n is close to 1, indicating that the mechanism corresponds to non-fickian diffusion (anomalous diffusion). These results justify the proposed mechanism for the first and second stages of this system and imply that the rate of diffusion is higher than the mobility of the polymer chain segment, favoring the erosion process [43].

After the controlled release tests, new micrographs were made from the treated surface of the wool fabric, Figure 7. It is possible to verify that some microcapsules have been ruptured and small holes are still observed, these were caused by the overlapping mechanism of diffusion and retention of the oil. The encapsulated material is protected

against adverse conditions, including the immersion in water, which has already been pointed out as being of capital importance in the application of oils in textiles [1, 22].

Figure 7. Scanning electron micrographs of citronella oil microcapsules (GA/GE) applied on wool fiber using the foulard process and the pad-dry-cure-technique and BTCA as cross-linking agent after 700 minutes of In vitro controlled release in water at 37 ^{o}C.

The results obtained in the *"in vitro*" experiments show that the designed system acts as a good device to control the delivery of Citronella oil applied to wool. The next step should be the performance of "*in vivo"* experiments using live insects with different characteristics, environmental conditions (temperature, moisture, etc.) and population to be eliminated. For every specific conditions and species, new devices could be designed to accomplish the desired final effects of the doses.

4. CONCLUSION

Microcapsules that protect the application of Citronella Oil have been obtained from the biocompatible and biodegradable system of polymers using complex coacervation methodology. The use of surfactant in the pre-emulsion stage allows obtaining a spherical geometry due to the previous ordering into the micellar phase formed. The fixation of these microcapsules in the wool fiber is possible using the chemical functionality of BTCA. The system remains physically stable after 400 min of contact with water under stirring conditions at 37 ºC.

The delivery profiles show a coupled mechanism, but not burst. The first stage (approximately 40% of delivery) shows a controlled Fickian mechanism associated with the spherical geometry, but anomalous diffusion occurs for higher release values of up to 100% of the encapsulated oil. This form of delivery means that there is the influence of the fiber chains and their interaction with the oil. The fittings applied to the experimental data through the Korsmeyer's and Higuchi's models allowed quantifying the coefficients of diffusion of oil in an aqueous medium and identifying the release mechanism.

The knowledge herein presented contributes with important information to the understanding of the rate of controlled release of active principles. It may additionally promote the use of oils and fragrances applied to textiles.

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